

The Geochemistry of As, Mo, Sb, and W in Natural Geothermal Waters, Iceland

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ABSTRACT

Arsenic, Mo Sb and W concentrations in Icelandic geothermal waters lie in the range 0.11-223 ppb, 0.15-48 ppb, 0.01-36 ppb and 0.14-78 ppb, respectively. The concentrations of As, Sb and W increases with increasing temperature, whereas Mo has irregular behaviour with temperature. Arsenic, Sb and W are mobile in the geothermal water. They are, however, less mobile than B and this is considered to be due to non-stoichiometric dissolution of the bulk rock with As, Sb and W being concentrated in the relatively insoluble titanomagnetite but B on a very soluble form. Molybdenum concentration in high-temperature waters is controlled by molybdenite solubility. Boiling of sulphide rich water leads to molybdenite supersaturation and precipitation whereas boiling of low sulphide water leads to insignificant molybdenite formation. This variable behaviour upon boiling is considered to be the main cause of the variable Mo concentration between geothermal areas in Iceland.

1. INTRODUCTION

The concentrations of As, Mo, Sb and W and processes controlling their chemistry in natural waters are of environmental interest. The enrichment of these elements in aqueous systems is useful in understanding the pollution problems. Further, As, Mo, Sb and W are predominantly transported as neutral aqueous species and oxy-anions by the waters and are found to be highly mobile in the geothermal environment (e.g. Arnórsson and Ívarsson, 1985; Arnórsson, 2003). They are, therefore, good indicators of extent of primary rock leaching and progressive water-rock reaction.

The concentrations of As, Mo, Sb and W in cold surface- and ground waters in Iceland are generally below 0.5, 1, 0.1 and 0.01 ppb (Arnórsson, 2003; Arnórsson and Óskarsson, 2004; Kristmannsdóttir, pers. comm.). Geothermal waters tend to be higher in all elements. In high temperature geothermal waters at converging plate boundaries As concentrations as high as 50 ppm have been reported although concentrations between 1 and 100 ppm is more typical (Bauer and Onishi, 1978; Stauffer and Thomson, 1984; Ballantyne and Moore, 1988; Sakamoto et al., 1988; Welch et al., 2000). The concentration in geothermal waters can reach 70 ppb for Mo (Arnórsson and Ívarsson, 1985; Koga, 1967), 300 ppb for W (Krainov, 1965) and 500 ppb for Sb (Brown et al., 2000). Seawater contains 1.7, 10, 0.2 and 0.1 ppb As, Mo, Sb and W, respectively (Krauskopf and Bird, 1994) and the concentrations of As, Mo, W and Sb in precipitation in Iceland are <10, <10, <20 and <5 ppt, respectively (Gíslason et al., 2000). Thus it is clear that all the elements are enriched in the geothermal waters compared to meteoric water.

Recent development of high resolution ICP-MS analysis permits rapid and inexpensive determination of many elements at sub-ppb levels in aqueous solution including As, Mo, W and Sb. The present study is based on such analysis in samples of geothermal springs and well discharges ranging in temperature from 20 to 300°C as well as in volcanic rocks in Iceland. The aim of the study is to determine the concentrations of As, Mo, Sb and W in the geothermal waters and quantify the processes influencing their chemistry in the water.

2. DATABASE AND DATA HANDLING

2.1 Database

A total of 62 samples were collected for the present study of geothermal well discharges and hot spring waters from Iceland with temperatures ranging from 20 to 300°C. Samples of hot spring waters were collected from the Geysir area, Landmannalaugar and Hveragerdi and geothermal well discharges from Krafla, Námafjall, Svartsengi and Reykjanes.

Major elements were analysed in the water samples and also in the steam phase where appropriate (?? Not clear). These include pH, CO₂, H₂S, B, SiO₂, Na, K, Mg, Ca, Cl, F and SO₄ in the waters and CO₂, H₂S, H₂, N₂, Ar, O₂, CH₄ in the steam. Detailed description of the sampling procedure and analytical methods is given by Arnórsson et al. (2000) and Gudmundsson and Arnórsson (2002).

Over 60 trace elements, including As, Mo, Sb and W were determined in the water samples by high-resolution ICP-MS at SGAB, Sweden. Samples were collected in acid washed polypropylene bottles and acidified with concentrated ultra clean HNO₃. The blank determination of As, Mo, Sb and W have been included in Table 1. The same trace elements were further analysed in selected volcanic rocks from Iceland by high-resolution ICP-MS at SGAB, Sweden and at Washington University, St. Louis.

The hot spring waters sampled are from both boiling and non-boiling springs. All the well samples are from wet-steam wells. Most of the geothermal fluids considered are dilute as the dissolved Cl content is less than 100 ppm. This is a characteristic of geothermal fluids of meteoric origin in the basalt terrain of Iceland. However, the geothermal fluids at Svartsengi and Reykjanes possess higher salinity due to the presence of a marine component. At Reykjanes the geothermal fluid is seawater (19,000 ppm Cl) and at Svartsengi it is a 2/1 seawater/meteoric water mixture (13,000 ppm Cl), but in all other waters the Cl content is less than 500 ppm.

2.1 Database

The WATCH speciation program of Arnórsson et al. (1982), version 2.1 (Bjarnason, 1994), was used to calculate the component concentrations and aqueous speciation distribution in the aquifer fluid of the wells and hot springs.

The thermodynamic database used for the speciation calculations is that given in Table 5 of Arnórsson et al. (1982) except for Al-hydroxy complex dissociation and gas solubility constants, which are from Arnórsson and Andréðóttir (1999) and Arnórsson et al. (1996), respectively. For the present study the thermodynamic properties of As, Mo, Sb and W were included in the program using hydrolyses constants calculated with the aid of SUPCRT92 program (Johnson et al., 1992) and using the slop98.dat data base and data on Mo reported by Arnórsson and Ivarsson (1985).

The primary advantage of WATCH program, compared to most other aqueous speciation programs, is the calculation of speciation of fluid in aquifers producing into wet-steam wells and boiling hot springs. The chemical composition of samples from non-boiling springs represents the composition of the waters in the producing aquifer. On the other hand, the water samples collected from the wellhead of wet-steam wells and boiling hot springs are not representative of the parent aquifer water, since steam loss and degassing have modified their chemical composition.

The WATCH program calculates the aquifer fluid composition and the aqueous speciation distribution of that fluid for wet-steam wells from analysis on water and steam samples collected at the wellhead. For these calculations boiling is usually taken to be adiabatic and no steam is generally assumed to be present in the aquifer beyond the depressurization zone around discharging wells. However, such conditions are not always met, at least when extensive boiling starts in the producing aquifer(s) of a well (Arnórsson et al., 1990). Transfer of heat from the aquifer rock to the flowing water may enhance its vaporisation, thus raising the enthalpy (steam to water ratio) of the discharge. Segregation of the flowing water and steam, which involves preferential movement of the steam into the well due to the relative permeability effect and capillary forces can also lead to excess enthalpy of well discharges (Arnórsson et al., 1990).

For the present study the aquifer fluid composition and speciation distribution for the wet-steam wells were calculated assuming the presence of equilibrium steam in the aquifer and excess discharge enthalpy of wells as a result of phase segregation (Arnórsson et al., 1990). The selected aquifer temperature, i.e. the temperature at which the aqueous speciation was performed, was derived from the average temperature values of the silica, Na/K and H₂S geothermometers in the case of Krafla and Námafjall (Gudmundsson and Arnórsson, 2002) but from the quartz geothermometer in the case of Svartsengi and Reykjanes.

For the boiling hot springs the pH was measured at room temperature within 48 hours of sampling. Upon storage, the pH has been observed to increase due to silica polymerisation. A method, based on measured monomeric Si concentration at the time of the pH measurement and conservation of alkalinity was applied to correct for these pH changes. This method has been observed to be successful at pH>9 as indicated by a very good ionic balance after the pH corrections. Using the corrected pH, the aquifer fluid composition and the aqueous speciation for the boiling hot springs were calculated with the WATCH program. The degassing was assumed to be 10%, 20% and 60% of maximum (equilibrium) degassing for Geysir area, Hveragerdi and Landmannalaugar, respectively. This assumption was based on the observation that these waters were generally highly supersaturated with calcite at the aquifer temperature suggesting CO₂ loss. The degassing

coefficients were selected because they yielded the best overall fit with calcite saturation for the respective areas. The aquifer temperature was calculated with the chalcedony and quartz geothermometers below and above 180°C, respectively.

3. DISTRIBUTION OF As, Mo, Sb AND W IN IGNEOUS ROCKS

The concentration of As, Sb, Mo and W in selected rock samples from Iceland are given in Table 1. The rock samples range in composition and type and include olivine-tholeiite, tholeiite, icelandite, dacite and rhyolite.

Table 1. Partial analysis of selected volcanic rocks in Iceland

No	B ppm	As ppm	Mo ppm	Sb ppm	W ppm
TR-130 ^a	1.01	0.09	0.46	0.017	0.12
NF6 ^b	0.67	0.12	0.65	0.038	0.15
sk2 ^b	1.65	<0.09	0.95	0.064	0.30
sk4 ^b	1.88	<0.09	1.36	0.091	0.47
sk10 ^b	2.25	0.61	2.15	0.075	0.59
IDAC ^c	1.59	0.41	1.13	0.040	0.33
A-5 ^d	1.52	0.65	2.57	0.045	-

^a ol-thol; ^b thol.; ^c dacite; ^d rhyolite

In basalts the As content ranges from 0 to 1.28 ppm with an average concentration in tholeiite of ~0.1 ppm. As is an incompatible element during magma evolution as indicated by a positive correlation with K₂O and Rb (Arnórsson, 2003). The Mo concentration ranges from 0.09 to 4.0 ppm for basaltic to silicic volcanism in Iceland with an average concentration of 1.1 ppm in tholeiite. Mo seems to be higher in silicic than basaltic volcanism. The W concentration in tholeiite was found to lie between 0.13 and 1.13 ppm with an average value of 0.38 ppm. For other rock types limited data are available. Tungsten is known to be incompatible in magmatic processes and is therefore assumed to be enriched in silicic rocks compared to basaltic. The Sb content was found to be lower compared to the other trace metals under study with values in the range 0.013-0.022 ppm in olivine-tholeiite, 0.018-0.091 ppm in tholeiite and 0.40-0.45 in dacite and rhyolite. Differences in Sb concentration are, therefore, insignificant between basaltic and silicic volcanism.

4. As, Mo, Sb AND W DISTRIBUTION IN WATERS AND THEIR SPECIATION

The concentrations of As, Mo, Sb and W in selected water samples are given in Table 2 and plotted as a function of temperature in Figure 1. The concentrations are those in the source aquifer.

The As concentration is observed to increase with increasing temperature from 0.1 to 10 ppb at t<100°C to 10-223 ppb at higher temperatures. The As concentration depends on both host rock composition and progressive water-rock interaction. In the Landmannalaugar area, which is hosted by silicic volcanism, the As concentration of the water is 10 times higher than at Hveragerdi, Krafla and Námafjall that are associated with basalt. Tungsten concentrations increase with increasing temperature with values between 0.1 and 10 ppb at t<100°C and between 1

Table 2. Selected elemental aquifer fluid composition calculated with the aid of the WATCH program (see text)

No	Location	t/°C	Cl ppm	B ppm	As ppb	Mo ppb	Sb ppb	W ppb
01-201	Geysir	233	92.1	0.78	62.6	30.37	2.90	20.5
01-207	Konungshver	226	93.2	0.77	61.6	33.46	3.29	21.8
01-208	Helludalur 1	30	20.6	0.11	2.02	8.24	0.025	2.05
01-236	Bólúhver, Landmannalaugar	126	173	1.15	16.9	0.15	6.04	38.4
01-241	Eyrarhver	160	441	4.50	223	5.15	27.1	77.9
01-244	Grænalaug	56	4.50	0.09	0.45	1.97	0.092	1.33
01-246	Landmannalaugar VII	18	22.2	0.20	2.83	7.12	0.092	0.16
02-204	(???)	65	36.2	0.17	0.37	0.89	0.033	3.81
02-206	Bólúhver, Hveragerdi	152	122	0.45	2.77	0.68	0.170	5.45
02-210	Spring in Hveragerdi village	197	135	0.47	4.44	1.12	0.348	6.25
02-219	Krafla, 12	275	88.4	1.04	26.3	1.70	0.129	7.20
02-227	Reykjanes, 11	287	18338	7.91	116	7.16	0.236	2.31
02-228	Svartsengi, 9	232	12861	7.13	55.22	7.14	0.590	0.66
	Blank				<0.05	0.02	<0.002	<0.002

and 80 ppb at $t > 100^\circ\text{C}$. Antimony concentrations are much lower with values ranging from 0.01 to 0.1 ppb at $t < 100^\circ\text{C}$ and 0.1 to 36 ppb at $t > 100^\circ\text{C}$. Both W and Sb show similar behaviour as that of As with rock composition and progressive water-rock interaction. They tend to be higher in waters associated with silicic rocks and waters that are more reacted. The Mo concentrations ranges from 0.1 to 50 ppb. They do not display any regular variation with temperature. The waters with low temperatures tend to be low in Mo as well as waters associated with dilute high-

temperature waters that are also high in sulphide. Saline waters and waters that are low in sulphide tend to have higher Mo concentrations.

The results of the speciation calculations indicate that As is present predominantly in the As(III) oxidation state with $\text{H}_3\text{AsO}_3(\text{aq})$ and H_2AsO_3^- being the dominant aqueous species, the absolute importance depending on the water pH and temperature. For Mo both HMoO_4^- and MoO_4^{2-} are

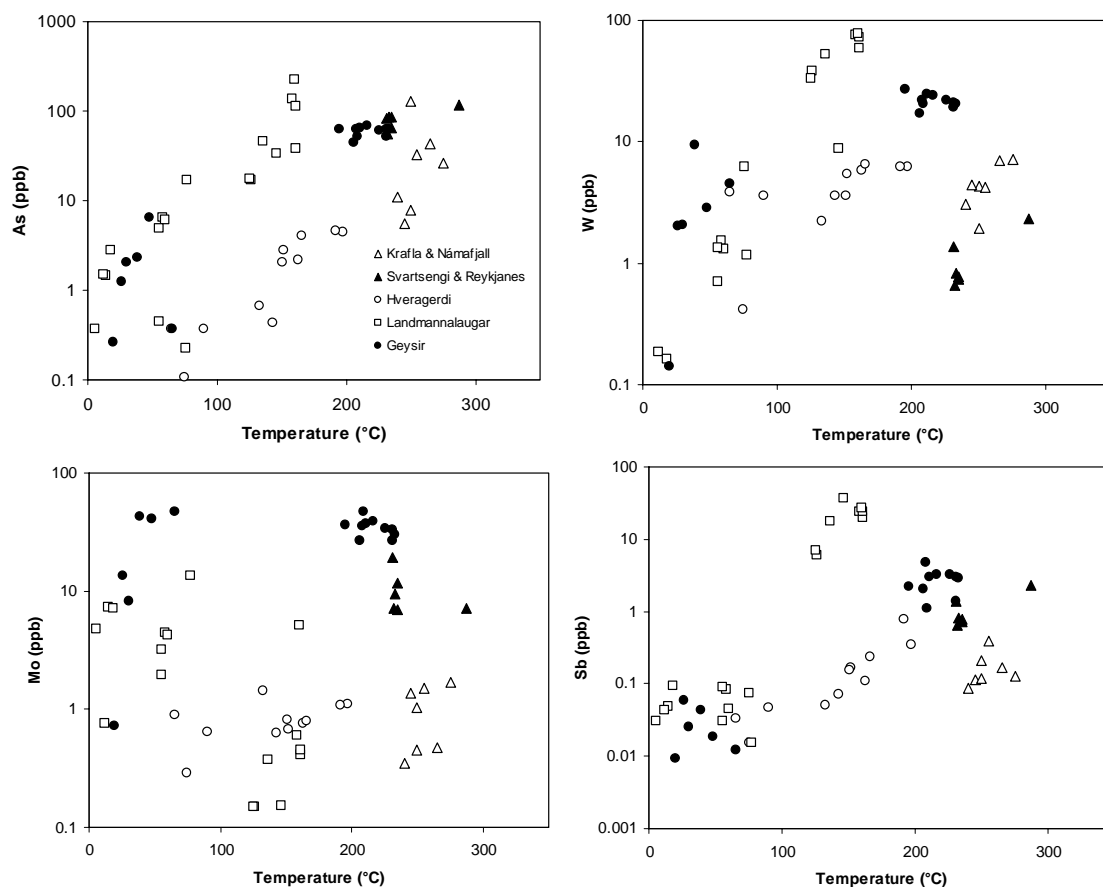


Figure 1. The relationship between As, Mo, Sb and W concentrations and temperature in aquifer waters in Iceland.

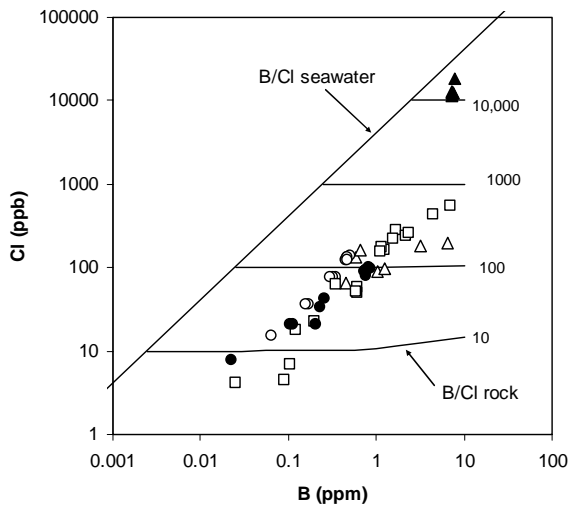


Figure 2. Relationship between Cl and B in aquifer waters in Iceland. The near vertical lines (which ones?) demonstrate the Cl and B evolution during the progressive basalt dissolution from the original source water that is characterised by Cl/B ratio similar to seawater. Basalts have much higher B/Cl ratio. Upon progressive rock dissolution the waters become successively enriched in B relative to Cl in the original unreacted water. The symbols refer to the legend in Figure 1.

important depending on the pH whereas WO_4^{2-} accounts usually for more than 90% of the total measured W concentration. The predominant form of Sb was observed to be $H_3SbO_3(aq)$ with $H_2SbO_3^-$ being only important in the most alkaline waters. As, Mo, Sb and W are, therefore, present as either neutral aqueous species or oxy anions in geothermal waters in Iceland. In reducing H_2S solutions, the thio complexes of As, Mo, Sb and W may play an important role (e.g. Erickson and Helz, 2000; Zakaznova-Iakovleva 2003). Such complexes were not incorporated in the speciation calculations due to limited data on their stability data.

5. PROGRESSIVE WATER-ROCK INTERACTION AND As, Mo, Sb AND W MOBILITY

For mobile elements that are not incorporated into secondary minerals, increased primary rock dissolution will lead to an increased elemental concentration in the fluid. Boron and Cl are known to behave as highly mobile elements in geothermal waters in Iceland (Arnórsson and Andrésdóttir, 1995). Therefore, the increased primary rock dissolution will increase the concentration of both Cl and B in the waters relative to the original Cl and B content of the parent water. This process is demonstrated in Figure 2. Geothermal waters in Iceland are of meteoric and seawater origin and the initial Cl/B ratio is fixed by the Cl/B ratio of seawater. The absolute Cl and B concentration, i.e. the original salinity, is however, variable. The Cl/B ratio of basalts is much lower (between 5 and 30 on molal basis) than that of seawater, so the progressive rock dissolution increases the B concentration in the waters relative to Cl. The rock derived B concentration in the water is a measure of extent of rock dissolution.

The relationship between As, Mo, Sb and W concentration with those of B are depicted in Figure 3. As, Sb and W

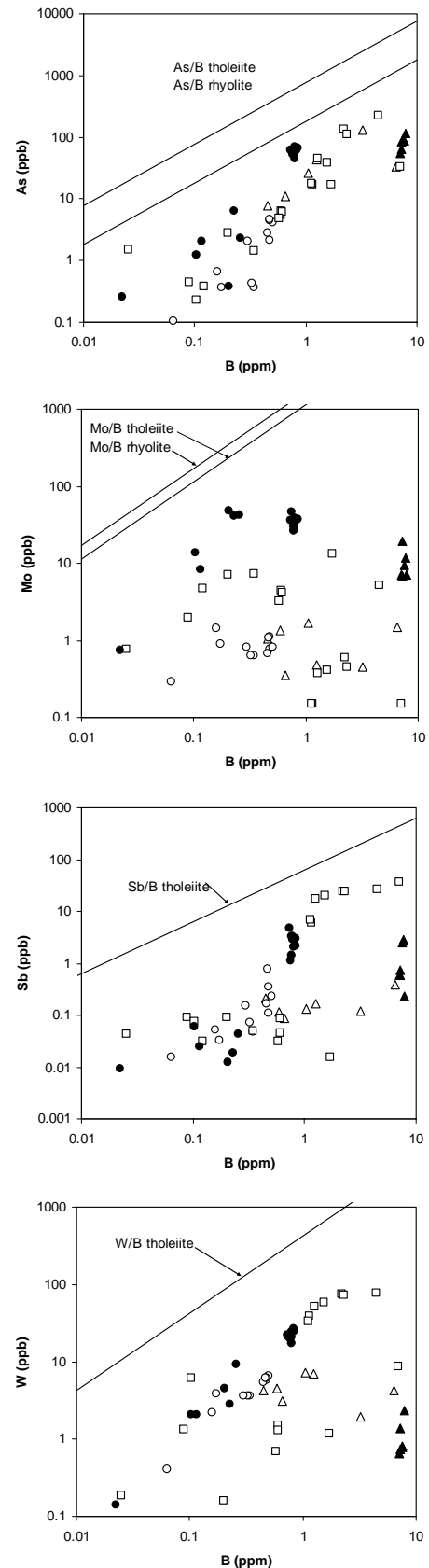


Figure 3. Aqueous As, Mo, Sb and W versus B concentration in aquifer waters. The lines represent the average basalt and rhyolite ratios. The symbols refer to the legend in Figure 1.

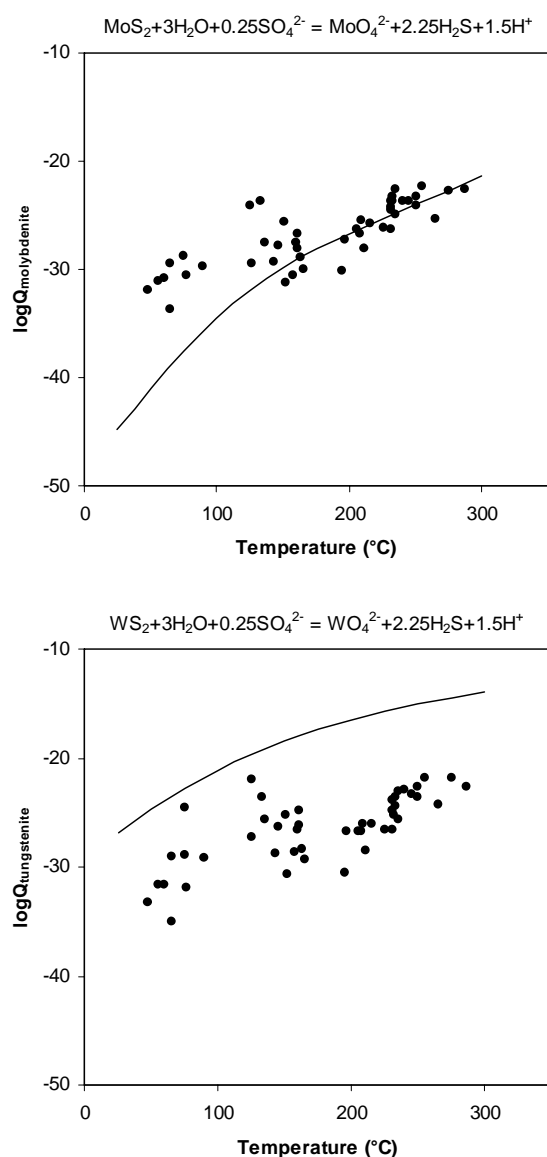


Figure 4. Molybdenite and tungstenite saturation state in geothermal waters.

act as mobile components as indicated by their increased concentrations with those of B. However, the As, Sb and W to B ratios are all considerably lower than the same ratios in basalt. Thus, As, Sb and W are released into the water in lower quantity than that of B. This is considered to be due to non-stoichiometric rock dissolution but not selective removal of As, Sb and W from solution relative to B. As, Sb and W are expected to be concentrated in the titanomagnetite of basalt (Esson et al., 1965) which have been shown to be stable in contact with geothermal waters in Iceland (Stefánsson et al., 2001). On the other hand, almost all the B is present in basalt in a very soluble form (Ellis and Mahon, 1967).

In sulphide rich high-temperature waters, Mo shows much lower mobility relative to B than As, S and W. In the Geysir area, the sulphide concentration is generally below 5 ppm and the Mo concentration is typically in the range 25 to 45 ppb. At Landmannalaugar, Krafla and Námafjall geothermal areas the total sulphide concentration ranges from 16 to 240 ppm, whereas the Mo concentration is in the range 0.4 to 14 ppb. In Figure 4 the saturation states for molybdenite and tungstenite are shown assuming that the

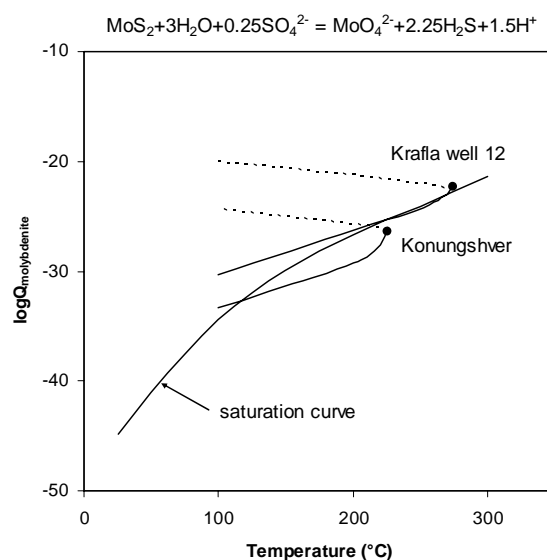


Fig. 5. The effect of boiling (solid line) and cooling (broken line) on molybdenite saturation state for two geothermal aquifer waters, Krafla well 12 and the Konungshver hot spring in the Geysir area. Maximum degassing was assumed in both cases.

H_2S/SO_4 redox couple controls the reduction of aqueous hexavalent Mo and W to tetravalent Mo and W. The solubility curves were calculated using thermodynamic data of minerals and aqueous species reported by Arnórsson and Ívarsson (1985), Robie and Hemingway (1995) and Shock et al. (1997). Despite considerable scatter of the data aquifer Mo concentrations at $t > 150^\circ C$ seems to be controlled by a close approach to equilibrium with molybdenite. Accordingly, this mineral controls the Mo mobility in the water. On the other hand, the waters are undersaturated with tungstenite which is more soluble than molybdenite. Accordingly, this mineral is not expected to be stable and does not therefore affect W mobility.

The effect of aqueous sulphide concentration on Mo mobility is considered to be related to the effects of boiling and cooling of the geothermal waters upon molybdenite saturation. The saturation state of molybdenite is highly dependent on pH and H_2S activity in addition to decreasing solubility with decreasing temperature. The effect of boiling and cooling is shown in Figure 5 for two samples: for well 12 at Krafla and the hot spring of Konungshver, Geysir area. The well discharge is characterised by low Mo content and high in H_2S concentration but the hot spring water is high in Mo and low in H_2S . For both Krafla well 12 and Konungshver, the waters become supersaturated upon conductive cooling. Boiling also leads to supersaturation at Krafla whereas insignificant molybdenite supersaturation results by boiling of the low sulphide waters emerging in Konungshver. Boiling and subsequent pH increase and H_2S transfer to the steam phase is an effective way of precipitating sulphide minerals whereas cooling is probably not effective. It is therefore concluded that the much higher Mo concentrations found in low sulphide boiling springs at Geysir is due to insignificant molybdenite precipitation during boiling in the upflow when boiling of sulphide rich fluids leads to molybdenite supersaturation and precipitation and subsequent Mo removal from solution.

5. CONCLUSIONS

The chemistry of As, Mo, Sb and W in geothermal waters from Iceland has been studied. The aquifer temperatures of the studied waters range from 20 to 300°C and the salinity is between <100 and 19,000 ppm Cl. The concentrations of As, Sb and W increase with increasing temperature. In low-temperature waters As, Sb and W are typically below 1, 10 and 0.1 ppb, respectively, whereas in high-temperature water values as high as 228, 36 and 78 ppb, respectively, are observed. The concentration of Mo varies irregularly with temperature ranging from 0.15 to 48 ppb. In the geothermal waters As, Mo, Sb and W are present as neutral aqueous species and oxy-anions. They, therefore, have a tendency to be mobile like other large anions. As, Sb and W act as mobile during water-rock interaction and their concentrations tend to increase with increasing primary rock dissolution. By contrast, Mo concentrations in high-temperature waters are controlled by molybdenite solubility. It is concluded that boiling of sulphide rich water leads to molybdenite supersaturation and subsequent precipitation of this mineral but boiling of low sulphide water leads to insignificant molybdenite precipitation. This is considered to explain the variable Mo concentrations in high-temperature geothermal waters

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